

PROTECTION OF THE ENVIRONMENT

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NEUTRALIZATION AND PURIFICATION OF ACIDIC WASTE WATERS CONTAINING HYDROFLUOROSILICIC ACID IN THE PRODUCTION OF ULTRAPURE QUARTZ

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A method for solid-phase neutralization of waste waters (in the production of ultrapure quartz) by dry caustic lime in a moving bed of the material is studied. This method will make it possible to obtain at the exit from the granulator a solid granular product convenient for subsequent processing (briquetting and drying for the needs of metallurgy or shipment). Advantages of this method over the liquid phase method are that there is no need for preparing milk of lime or filtering finely disperse residue, the volume of wastes waters is smaller and a flux is obtained in a granular form.

Key words: quartz, waste waters, neutralization, granulation, fluorspar, fluorite, lime.

The technology for obtaining ultrapure quartz at the final stage of purification includes etching of the quartz in hydrofluoric acid. The reaction goes to completion (to exhaustion of HF). Products of the reaction are purified quartz, which is the solid part, and waste waters, comprising the production waste requiring recovery or conditioning for safe storage. In practice the waste waters from the production of ultrapure quartz contain > 99% hydrofluorosilicic acid (HFSA).

The acid concentration is 22 – 24% in terms of H_2SiF_6 . The conventional technology for safe disposal of acid comprises neutralization by milk of lime and shipment of the resulting alkaline pulp to a tailing dump [1, 2].

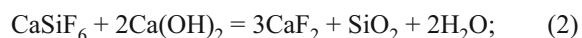
The process of neutralization by lime results in the formation of a solid phase whose main component CaF_2 (fluorite) is a marketable product in demand, for example, as a flux for the metallurgy industry.

The metallurgical grades of fluorite product must contain > 65% CaF_2 , but the technical conditions of application require large chunks of fluorite (the fraction of pieces smaller than 50 mm must be less than 10%). Obtaining the required purity of the raw material together with adequate nodularity of the fluorite material is a quite difficult problem, and furthermore metallurgical grade fluorspars are quite scarce raw materials. However, most of the material proposed for realiz-

ing fluorspar is small-grain. The grains can be enlarged by clumping and briquetting of fluorspar concentrates, but this simply makes the end product more expensive.

Scientific research and the analysis of published work have shown that the products of neutralization of HFSA can be used as flux for making steel. Flux is necessary in a solid dry form and must have a definite granulometric composition.

The products of neutralization comprise a mixture of low-solubility compounds — $3\text{CaF}_2 + \text{SiO}_2 + \text{excess Ca(OH)}_2$. Excess Ca(OH)_2 is necessary to reach pH = 8 – 9, at which the disproportionation reaction of CaSiF_6 formed at the first stage proceeds:



the complete reaction is



The following are required to obtain ready flux by *conventional neutralization of waste waters* by milk of lime: a unit for preparing milk of lime from caustic lime, a neutralizing reactor, a unit of separating phases (filtration, centrifuging), a drying unit and a briquetting unit. In addition, there arises the serious problem of purifying waste waters to the

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Fig. 1. Exterior view of granules obtained during solid-phase neutralization of waste waters.

waste water discharge norms with respect to fluorine and silicon.

The *solid-phase variant of neutralization* of waste waters by caustic lime in a mobile bed of material was investigated. In this case a solid granular product is obtained at the exit from the granulator; this product is convenient for subsequent processing (briquetting and drying for metallurgy or shipment).

The advantages of this method over the liquid-phase variant are that the preparation of milk of lime or the filtration of finely disperse precipitate are not necessary, there is a significant reduction in the volume of waste waters and the flux is produced in granular form.

The experiments were performed in a laboratory granulator with a 230 mm in diameter cup with 40 mm high upturn along its entire perimeter. The cup is connected through a reduction gear to an electric motor, which puts the cup into rotation. The entire apparatus is mounted and secured to a metal base, making it is possible to regulate the inclination of the cup of the granulator and find the optimal regime for rolling different materials.

A weighed amount of the neutralizing agent CaO was placed into the granulator cup and a HFSA solution was introduced in portions into the material at the same time that the cup was put into motion. The neutralization reaction proceeded as the acid was added. The reacting mass formed was molded into granules (Fig. 1). If necessary, to secure a prescribed temperature for the reacting mass the granulator cup was additionally heated. The granules obtained were kept in air or in a drier at temperature 80 – 100°C until a constant mass was reached, after which their physical and chemical properties were determined.

The work was performed using a complex of analytical tests. Modern physical-chemical methods of analysis were used to identify the products: x-ray phase analysis, scanning

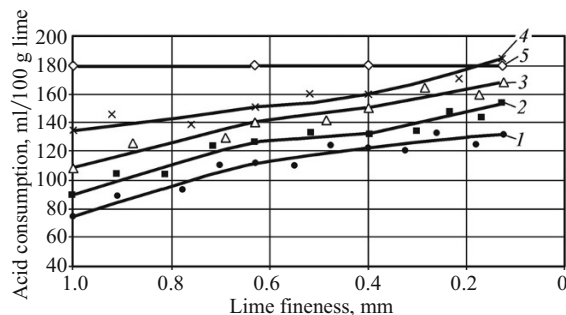


Fig. 2. Effect of the lime fineness and the process temperature on waste water consumption. Lime consumption: 1) 20°C; 2) 40°C; 3) 50°C; 4) 60; 5) stoichiometric rate (norm 100%).

electron microscopy, atomic-absorption analysis and differential-thermal analysis (DTA).

Two solutions were studied: spent acid from the first decantation with HFSA content about 24 wt.% (acid density 1.21 g/cm³) and a combined solution of acid from the first decantation and washing waters with HFSA concentration about 12 wt.% (acid density 1.10 g/cm³).

Caustic lime CaO (IF-2 grade) was the neutralizing agent: grade 2, content of main component 85.4%, producer Serov Ferroalloy Works.

INVESTIGATIONS OF SOLID-PHASE NEUTRALIZATION OF FIRST-DECANTATION SOLUTION

Solid-phase neutralization is based on the fact that in the course of an exothermal heterogeneous process some water passes into the gas phase and some is bound by the products of reaction both physically and chemically in the form of capillary moisture, which acts as a binder in granules, in the first case and in the form of crystal hydrate moisture in the second.

The fineness of the neutralizing agent used and the temperature in the reaction zone were studied as factors affecting the organization of the process.

The lime was comminuted in a laboratory vibrating pulverizer and sieved (sieve openings smaller than 1, 0.63, 0.4 and 0.125 mm) on an electric Ro-Tap. Next, materials of different fineness were studied by the method described above. The results obtained are presented in Table 1 and Fig. 2.

The standard consumption of the neutralizing agent (norm) per unit volume of the waste water was determined as follows: waste water (hydrofluorosilicic acid solution) was added to pH = 7 – 8.

The data show that the waste water consumption depends on the fineness of the neutralizing agent and the temperature of the medium. It is obvious that the consumption of water wastes tends to increase, and under optimal conditions the plots approach as closely as possible to the theoretical level

of consumption (norm). The smaller the fineness of the lime (limestone) and the higher the temperature of the medium, the higher the waste consumption is. This can be explained by the fact that as the particle size decreases, the contact surface area between the material and acid increases and therefore the diffusion stopping at the solid – liquid boundary decreases, which given the limited process time (15 – 20 min) results in high completeness of the reaction. The temperature factor affects the kinetics of the neutralization process.

At the end of the granulation process the granules had an alkaline reaction.

The overconsumption of the reagent was calculated as the difference (expressed as a percentage) between the normal consumption ('norm') determined in the course of the liquid-phase process and the actual consumption occurring in the course of the experiment.

Enlarged tests for solid-phase neutralization of a 24% solution of HFSA by lime were performed on the basis of laboratory studies. The main indices of the process are presented in Table 2.

In the enlarged experiments the hardness of the granules obtained with 24% neutralization of the hydrofluorosilicic acid by lime was adequate for use as a flux (10 kg/cm²).

To determine the residual lime content 10 g samples of the granules were flooded with water, held for 24 h and re-pulped and an indicator was added and titration performed.

The results of an analysis of the chemical composition of the granules obtained in the course of the solid-phase neutralization (fineness 0.1 mm) are presented in Table 3.

The data in Table 3 show that the degree of completion of the neutralization reaction increases with increasing temperature in the reaction zone during granulation. The product obtained at neutralization temperature 50°C and CaO consumption rate 0.62 kg/dm³ of waste water the product contains 65.9% CaF₂. In terms of the technical conditions it corresponds to FG-65 grade flux.

STUDIES OF SOLID-PHASE NEUTRALIZATION OF COMBINED DECANTATION

The difficulty of processing combined decantation is due to its about 2.3 times higher water content. The excess water cannot be removed by increasing the temperature of solid-phase neutralization because the HFSA evaporates. One variant remains — increasing the mass of the solid phase introduced into the process.

Laboratory studies performed with a 24% HFSA solution established that the fineness of the neutralizing agent and the temperature of the medium affect the granular neutralization

TABLE 1. Solid-Phase Neutralization Indices

<i>t</i> , °C	Lime fineness, mm	Lime consumption,* kg/dm ³ waste waters	Lime overconsumption,* %	pH	Granule properties		
					Moisture, %		Granule hardness, g/cm ²
					Drying in air	Drying at 100°C	
20	> 1	1.25	56.0	10 – 11	20.0	22.0	< 1
	> 0.63	0.89	38.4		23.0	24.4	< 1
	> 0.4	0.82	32.1		25.0	27.5	1 – 3
	> 0.125	0.76	27.3		30.0	31.0	1 – 3
30	> 1	1.11	50.4	10 – 11	21.5	23.0	< 1
	> 0.63	0.79	35.7		24.0	24.5	< 1
	> 0.4	0.76	27.3		25.8	27.3	1 – 3
	> 0.125	0.65	15.25		32.0	33.0	1 – 3
40	> 1	0.93	40.6	10 – 11	21.0	22.0	< 1
	> 0.63	0.71	22.9		23.6	25.4	< 1
	> 0.4	0.67	17.4		27.0	28.0	1 – 3
	> 0.125	0.60	7.6		32.0	32.0	1 – 3
50	> 1	0.75	26.2	10 – 11	26.8	27.2	< 1
	> 0.63	0.67	17.4		30.5	31.0	< 1
	> 0.4	0.62	12.0		30.5	32.5	1 – 3
	> 0.125	0.54	–		32.0	33.0	1 – 3

* CaO consumption 0.55 kg/dm³ waste water was adopted as the norm (zero overconsumption).

TABLE 2. Indices of the Granulation Process (Enlarged Experiments)

<i>t</i> , °C	CaO consumption,* kg/dm ³ waste waters	CaO overconsumption, %	Efficiency in terms of		
			waste, dm ³ /h	CaO, kg/h	granules, kg/h
20	1.20	45	9.5	11.4	20.9
40	0.74	34	14.8	11.4	26.2
50	0.62	12	18.2	11.4	23.68

* The value 0.55 kg/dm³ (zero overconsumption) is taken as the normal consumption level.

TABLE 3. Results of Chemical Analysis of the Granules

CaO consumption, kg/dm ³ acid	<i>t</i> , °C	Granule composition, %			
		CaF ₂	CaO		SiO ₂
			Spectral analysis	Titration	
0.76	20	43.4	45.0	44.5	11.0
0.60	40	59.0	27.0	22.0	14.0
0.54	50	64.7	15.3	14.0	17.0
0.74*	40	55.4	30.0	31.0	14.2
0.62*	50	65.9	18.0	19.0	15.8

* Enlarged experiments.

TABLE 4. Process Indices for the Solid-Phase Neutralization of Combined Decantation

Experiment no.	Batch composition, %		CaO consumption, kg/dm ³ waste water	CaO overconsumption, % of norm	pH
	CaO	Recycle			
CaO norm			0.26	0	8
1	100	0	0.71	172.3	12
2	5	95	0.06	-76.9*	1
3	10	90	0.12	-53.8*	3
4	15	85	0.18	-30.8*	6
5	20	80	0.24	-7.7*	7
6	25	75	0.30	8.8	12

* The minus sign (–) signifies that more HFSA was consumed for the formation of granules than required according to the norm.

TABLE 5. Results of the Chemical Analysis of Granules

Experiment no.	CaO in batch, %	Granule composition, %			SiO ₂
		CaF ₂	CaO		
			Spectral analysis	Titration	
1	100	35.8	38.7	40.0	13.4
2	5	63.9	*	*	17.2
3	10	74.0	*	*	20.4
4	15	75.0	*	*	20.9
5	20	75.1	*	*	21.0
6	25	69.7	2.8	2.0	19.0

* The CaO excess was determined only for the granules in the experiments Nos. 1 and 6, where pH ≥ 8.

process. On this basis the following *indices of the process of neutralization of a combined decantation* were chosen:

- lime fineness < 0.4 mm;
- temperature of the medium 50°C;
- process time 20 min.

The investigations in solid-phase neutralization of a 12% HFSA solution included the following basic steps:

- neutralization by lime;
- neutralization by lime with a recycled material added — the product of solid-phase neutralization.

The fine fraction of the granules obtained during the neutralization of a 24% HFSA solution and comminuted to fineness < 0.4 mm was used as the recycled material. Subsequently, the recycled material was the basis for obtaining

granules during the neutralization of the combined decantation with the addition of 5, 10, 15, 20 and 25 wt.% lime.

The investigations showed that the use of pure lime results in colossal overconsumption compared with the norm (Table 4) and, most importantly, the production of unconditioned (in terms of CaF₂ content) product (Table 5).

The optimal results (neutralized granules with low lime consumption) were obtained with the ratio CaO : recycle = 25 : 75. Their CaF₂ content corresponds to the norms for metallurgical fluxes (FK-25, FG-65 grades).

CONCLUSIONS

1. It was shown that solid-phase neutralization of HFSA by caustic lime is possible in principle.

2. It was determined that the milling fineness of the reagent and the temperature in the reaction zone affect the completeness of the neutralization reaction.

3. Neutralization by calcium oxide from the first decantation (24% HFSA solution) makes it possible to obtain a granular product with content ≥ 65% CaF₂, corresponding to the FG-65 metallurgical flux grade.

4. Neutralization of a combined decantation (12% HFSA solution) with a similar product being produced is possible by a batch consisting of lime and recycled product in the ratio CaO : recycle = 25 : 75.

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